UNITED STATES DEPARTMENT OF COMMERCE • Maurice H. Stans, *Secretary*
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, *Director*

Standard Reference Materials:

Preparation and Evaluation of SRM's 481 and 482

Gold-Silver and Gold-Copper Alloys for Microanalysis

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PREFACE

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are "well-characterized mate- rials, produced in quantity, that calibrate a measurement system to assure compatibility of measurement in the nation." SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. In many industries traceability of their quality control process to the national measurement system is carried out through the mechanism and use of SRM'S. For many of the nation's scientists and tech- nologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the *NBS Special Publication− 260 Series* is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on all phases of the preparation, measurement, and certification of NBS-SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. It is also hoped that these papers will provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery,price, and so forth will receive prompt attention from:

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J. Paul Cali, Chief
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PREPARATION AND EVALUATION OF SRMIS 481 AND 482 GOLD-SILVER AND GOLD-COPPER ALLOYS FOR MICROANALYSIS

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The reasoning behind the choice of the systems Au-Ag and Au-Cu for SRM'S. and their suggested uses are described., We also report on the preparations of the materials, their chemical analysis, the tests performed to ascertain macroscopic and microscopic homogeneity, and on relative x-ray intensity measurements at various x-ray lines and voltages., A descrip-tion of the instrumentation (matrix scanner), techniques, and programs employed in the homogeneity studies, as well as tables and graphs of the x-ray intensity measurements, are appended.

Key words: Alloys; corrections; electron probe; homogeneity; matrix scanner; microanalysis; quantitative analysis; standard reference materials; x-ray emission.

1. INTRODUCTION

A. Requirements for Standard Reference Materials

Although the foundations for a theoretical method of calculating correction factors for quantitative electron probe microanalysis were established in 1949 [1][1], tests of this method, performed a few years ago on specimens of known composition, raised considerable question concerning capabilities of the electron probe microanalyzer as a quantitative tool [2-4]. It became quite evident that various practical techniques proposed for calculating the corrections [5-10] were in considerable disagreement and that in many cases all proposed procedures failed to properly correct the exp-. mental data obtained by experienced investigators. The re- sulting analytical errors frequently exceeded 10|jpercnt| relative A detailed analysis of these tests [3] suggested that the following potential sources of error may be responsible for these failures:

1. Some of the test specimens of presumably well knc- composition may have been poorly characterized on a macroscopic scale or be microscopically inhomogeneous.
2. Although the fundamentals of the generation of x rays by electron excitation are well known, there are uncertain in parameters and constants − such as the x-ray absorption coefficients − which adversely affect the accuracy of the method. The resulting uncertainties may be particularly large if the instrument conditions have been chosen injudiciously [3, 11-14].
3. Lack of adequate computational facilities has frequently prompted the investigator to use simplified calculation procedures which may also introduce error.

Figures in brackets indicate references beginning on p. 38

In order to improve the accuracy of the correction pro- cedures for electron probe microanalysis, it is thus necessary to obtain carefully prepared, microscopically homogeneous, and chemically analyzed standard materials. The measurement under carefully controlled conditions of x-ray emission intensities from these standards, including all necessary correction calculations [15], will permit an empirical adjustment within the precision of the measurement of those factors which are affected presently by uncertainty. Once these factors have been established, the standard reference materials will enable the analyst to test the accuracy of his measurement technique by comparing the relative x-ray intensities he obtains from such materials with those obtained by other operators under carefully defined operating conditions.

The Standard Reference Materials SRM 481 and 482 were selected, prepared, and tested in such a manner as to satisfy[2] the requirements indicated in Part 2 of this report SRM 481 consists of a series of gold-silver alloys, and SRM 482 a series of gold-copper alloys, both in nominal steps of 20 weight percent and including the pure metals. We will describe the reasons for choosing these particular alloys, their preparation and their characterization, and we will report the results of some x-ray measurements performed on them
(See Appendix 1).

B. Choice of Systems

SRM's 481 and 482 contain the elements of atomic numbers 29, 47, and 79, and therefore represent a good cross-section through the range of higher atomic numbers. For copper,

[2] An additional material of this type, SRM 480, which has a nominal composition of W80-Mo20 has been issued. It is described in NBS publication 260-16.

Table 2. Au–Ag Alloys SRM 481
Big–beam determinations of concentrations and standard deviations
on homogeneity test slices

Slice[a]		Au20–Ag80		Au40–Ag60		Au60–Ag40		Au80–Ag20	
		Ag	Au	Ag	Au	Ag	Au	Ag	Au
1	C_b	0.7829	0.2228	0.5992	0.4019	0.4000	0.5972	0.2006	0.8007
	s.d.	.0042	.0057	.0015	.0004	.0026	.0058	.0001	.0018
2	C	.7726	.2249	.6010	.3972	.3972	.6037	.1991	.7966
	s.d.	.0033	.0032	.0025	.0001	.0009	.0020	.0009	.0018
3	C	.7725	.2239	.5985	.4027	.3968	.6045	– –	– –
	s.d.	.0009	.0004	.0045	.0013	.0006	.0040	– –	– –
4	C	.7750	.2267	.5988	.3979	.3999	.6016	.1991	.8042
	s.d.	.0011	.0028	.0001	.0031	.0074	.0012	.0016	.0028
5	C	.7761	.2272	.5990	.4018	.4019	.5957	– –	– –
	s.d.	.0040	.0023	.0019	.0015	.0004	.0011	– –	– –

[a] Homogeneity test slices are transverse sections selected at widely separated longitudinal test locations. The number scheme for locations along the wire is: 1 − top; 2 through 4 − intermediate; 5 − bottom.

[b] Standard deviations estimated by the range method. See reference 19.

Table 3. Au–Cu Alloys SRM 482
Big–beam determinations of concentrations and standard deviations
on homogeneity test slices

Slice[a]		Au20–Cu80		Au40–Cu60		Au60–Cu40		Au80–Cu20	
		Cu	Au	Cu	Au	Cu	Au	Cu	Au
1	C_b	0.7978	0.1998	0.5972	0.3988	0.3971	0.6056	0.1977	0.7987
	s.d.	.0018	.0008	.0013	.0010	.0005	.0013	.0002	.0013
2	C	.7999	.2022	.5995	.4016	.3959	.6025	.1982	.8027
	s.d.	.0018	.0005	.0017	.0015	.0010	.0014	.0003	.0004
3	C	.7979	.2018	.6010	.4027	.3961	.6028	.1989	.8031
	s.d.	.0005	.0011	.0013	.0012	.0010	.0017	.0003	.0008

[a] Homogeneity test slices are transverse sections selected at widely separated longitudinal test locations. The number scheme for locations along the wire is: 1 − top; 2 − intermediate; 3 − bottom.

[b] Standard deviations estimated by the range method. See reference 19.

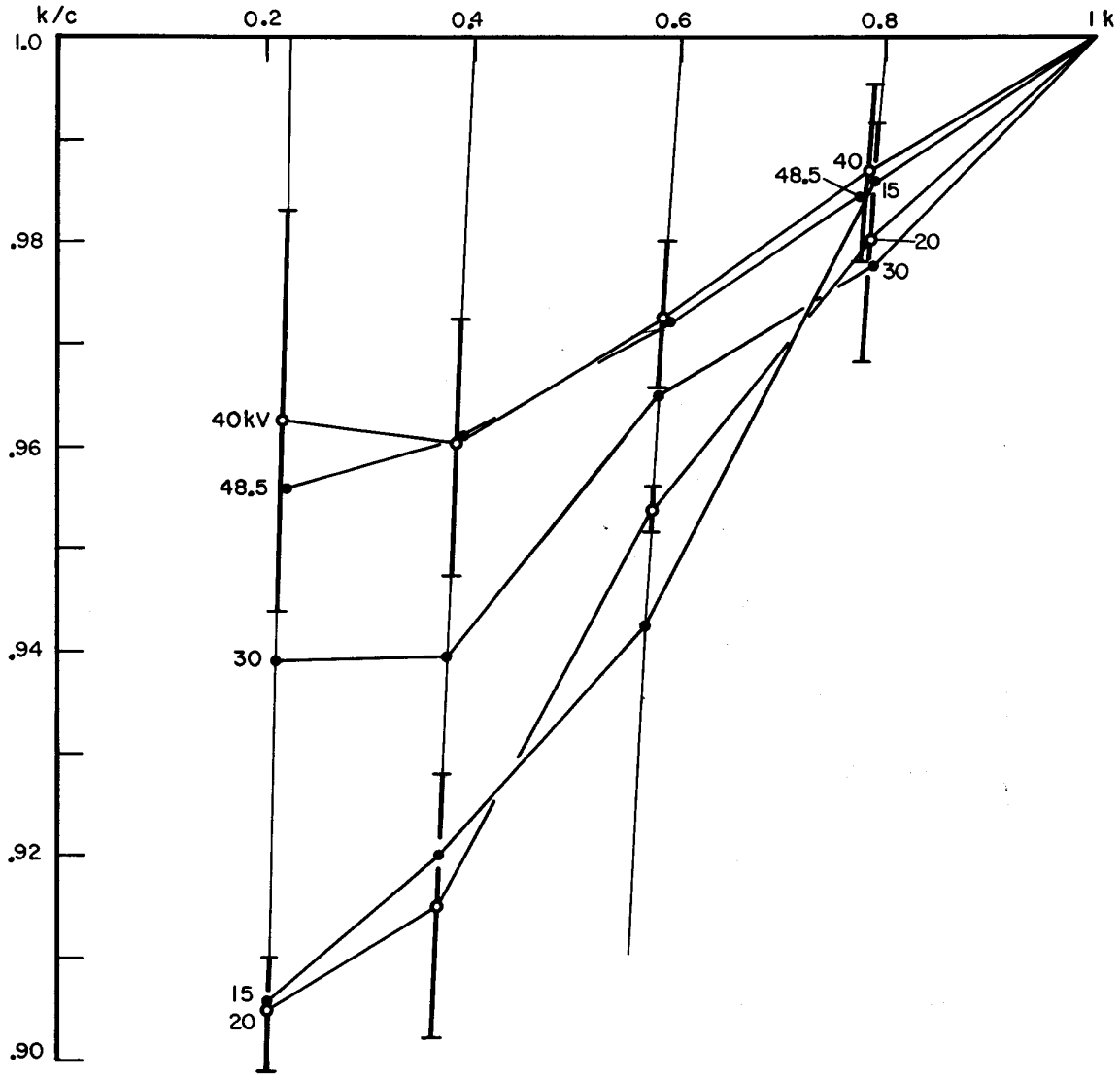

Figure 5. Experimental results on SRM 481 (Au-Ag) for AuLα_1. Bars in Figures 5 through 13 indicate ± 1 σa flanges. Points without bars represent single determinations. The numerical values of the data presented in these figures are listed in Tables 9-16.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material 481
Gold-Silver Wires for Microprobe Analysis

These standard reference materials are designed for use in quantitative elemental microprobe analysis. Although the selection of this particular system was circumscribed by the requirements of standard reference materials for electron probe microanalysis, the materials will be equally useful for other micro techniques. Accurate chemical characterization and the achievement of homogeneity on a microscopic scale was given special emphasis.

SRM 481 wire	Color code	Nominal comp	Cominco American[a]	U.S. Bureau of the Mint[b]		NBS[c]		Average Value[d]	
			Au	Au	Ag	Au	Ag	Au	Ag
			Percent by weight						
A	Gold	Au100	---	---	---	---	---	100.0_0	---
B	Gray	Au80–Ag20	80.00	80.02	20.00	80.13	19.93	80.0_5	19.9_6
C	Yellow	Au60–Ag40	60.01	60.11	39.85	60.04	39.98	60.0_5	39.9_2
D	Blue	Au40–Ag60	39.99	40.03	59.90	40.06	59.96	40.0_3	59.9_3
E	Red	Au20–Ag80	22.42	22.42	77.59	22.46	77.56	22.4_3	77.5_8
F	Silver	Ag100	---	---	---	---	---	---	100.0_0

[a] The fire assay method was employed for the determination of Au by Cominco American.

[b] At the U.S. Bureau of the Mint, Au was determined by fire assay and Ag was determined by titration as AgCl.

[c] At NBS, Au was determined from the residue after treatment of the alloys with HNO_3. The Au residue was dissolved in aqua regia, filtered, the Au precipitated by sulfurous acid, and weighed. Ag was determined gravimetrically as AgCl in all four alloys, and also coulometrically in the 80 percent Ag alloy.

[d] The results of individual laboratories agree within a range of ± 0.1 percent absolute from the average values. The agreement between results by the different methods and analysts, and the summation of results close to 100 percent for each binary alloy, indicate that the averages are free from significant bias.

The set of standard reference materials, SRM 481, consists of six wires each having a diameter of approximately 0.5 mm and a length of approximately 5 cm. For identification, the four alloy wires were covered with an easily removable colored coating.

The overall direction and coordination of technical measurements leading to certification were performed under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these standards were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
February 14, 1969

(over)

W. Wayne Meinke, Chief
Office of Standard Reference Materials

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10 X 10 MATRIX SCAN FOR 60 AU 20 AG 20 KV 3

                    CORRELATION GRAPH

ELEMENT 1 IS PLOTTED ON THE ORDINATE (VERT) AND ELEMENT 2
IS PLOTTED ON THE ABSCISSA (HORZ).
FOR EACH AXIS THE SCALE IS FROM -1.5% TO +1.5%.
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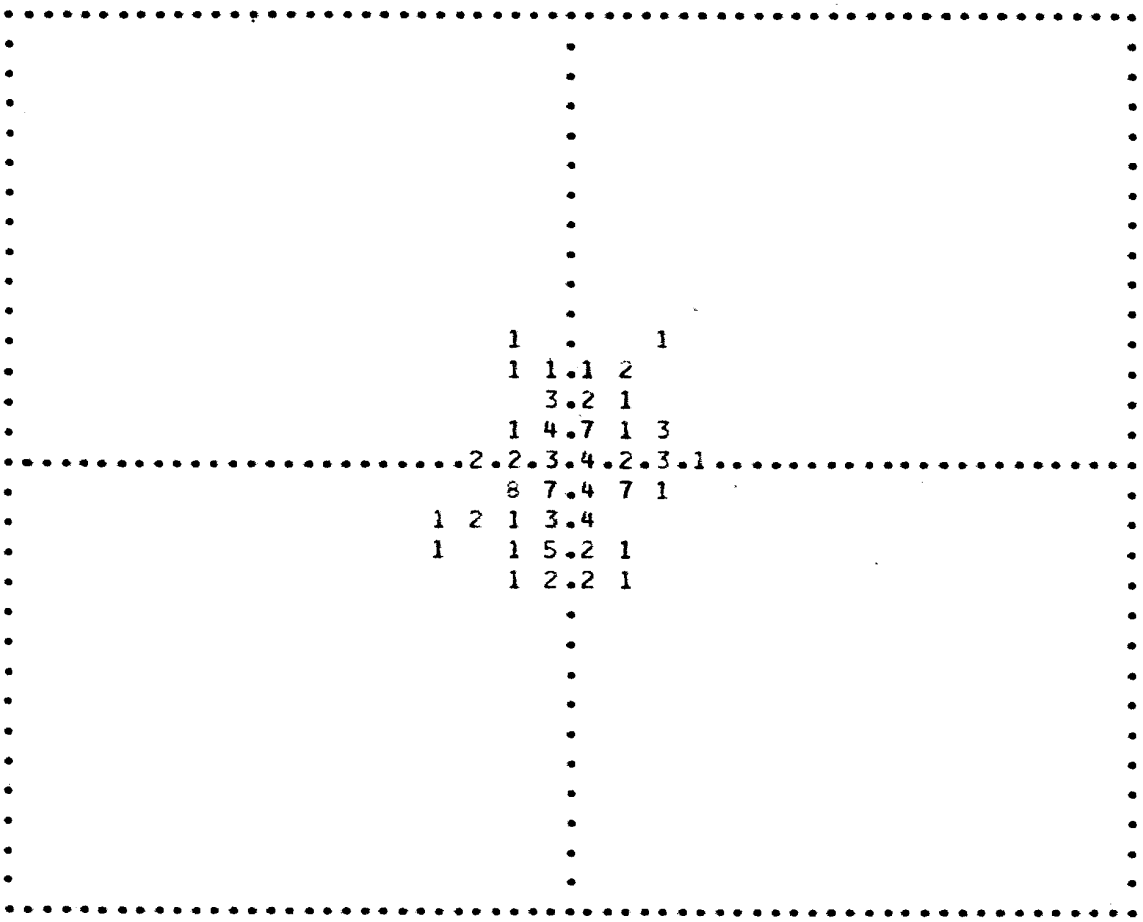

Figure 22. Correlation graph for the case given in Figure 17. Deviations from the mean Ag concentration are plotted on the ordinate while the deviations from the mean Au concentration are plotted on the abscissa. Deviations for neither element exceed 0.004, indicating good homogeneity.